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## Griffiths-like phase in manganese intercalated tantalum disulfide and the 3-dimensional Ising model

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GRIFFITHS-LIKE PHASE IN MANGANESE INTERCALATED TANTALUM DISULFIDE  
AND THE 3-DIMENSIONAL ISING MODEL

A Thesis Submitted  
in Partial Fulfillment  
of the Requirements for the Designation  
University Honors with Distinction

Paul White  
University of Northern Iowa  
May 2021

This Study by: **Paul White**

Entitled: **Griffiths-like Phase in Manganese Intercalated Tantalum Disulfide and the 3-dimensional Ising Model**

has been approved as meeting the thesis or project requirement for the Designation University

**Honors with Distinction**

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Date	Dr. Paul Shand, Honors Thesis Advisor, Physics Department

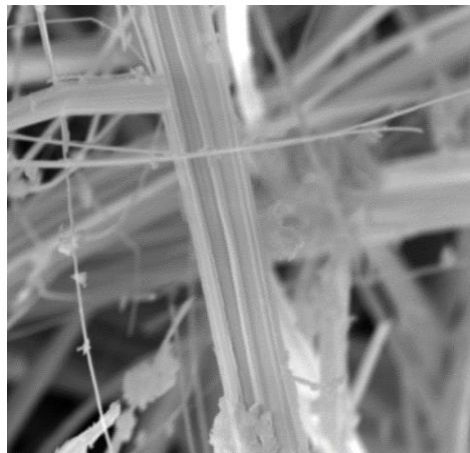
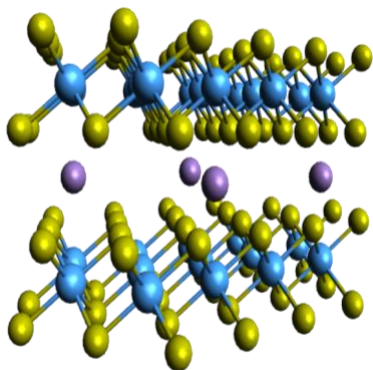
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Date	Dr. Jessica Moon, Director, University Honors Program

## **Introduction**

Transition metal dichalcogenides have gained increasing interest due to properties that make them highly attractive for fundamental studies of novel physical phenomena and for applications ranging from nanoelectronics and nanophotonics to sensing and actuation at the nanoscale.<sup>[1]</sup> The material described in this work is composed of layers of tantalum sulfide between which manganese was deposited. The number of manganese atoms per tantalum atom is called the concentration,  $x$ . In the research that was conducted for this thesis, the Griffiths Phase of crystalline bulk  $\text{Mn}_{0.23}\text{TaS}_2$  and the 3-dimensional Ising model was investigated.

In order to understand the significance of this study, the following information must be understood: the structure of the material and the basic properties of different kinds of magnetism.

The basic structure of the material being used throughout this project is shown on the left side of Figure 1. The entire structure, crystalline or nanostructured, is formed from this basic structure; one layer of manganese seated, or intercalated, between layers of tantalum disulfide. The manganese atoms control the magnetic properties of the entire material. The amount of manganese within these layers also determines the exact type of magnetism that the material will demonstrate. When the basic structure on the left side of Figure 1 is extended horizontally and repeated vertically, the structure produced is called crystalline. Alternatively, wrapping this basic structure around in the shape of a cylinder forms a nanotube—the fundamental building block of nanostructured samples. An example of the nanostructured material is shown on the right side of Figure 1.



*Figure 1. Left- crystal structure of  $Mn_xTaS_2$  where Yellow=Sulfur, Blue=Tantalum, Purple=Manganese*

*Right- A picture of a nanostructured sample taken with a scanning electron microscope. Taken by Payton Burken, Physics Dept. University of Northern Iowa.*

Within this work, magnetization and magnetic susceptibility will be mentioned continually. First, the magnetization of a sample is the total magnetic moment produced by the sample. In a bar magnet, the magnetic moment points in the direction from the south pole to the north pole (within the magnet), and its numerical value determines the strength of the magnet. The magnetization is calculated by adding together the strength of each of the atomic magnetic moments (due to the manganese) comprising the sample. The magnetic field produced by a single atom is comparable to that of a bar magnet in structure, only on the atomic scale. Secondly, the magnetic susceptibility is a measure of the response of a material to an applied magnetic field. The magnetic susceptibility  $\chi$ , can be expressed in equation 1 where M is the magnetization and H is the applied field.

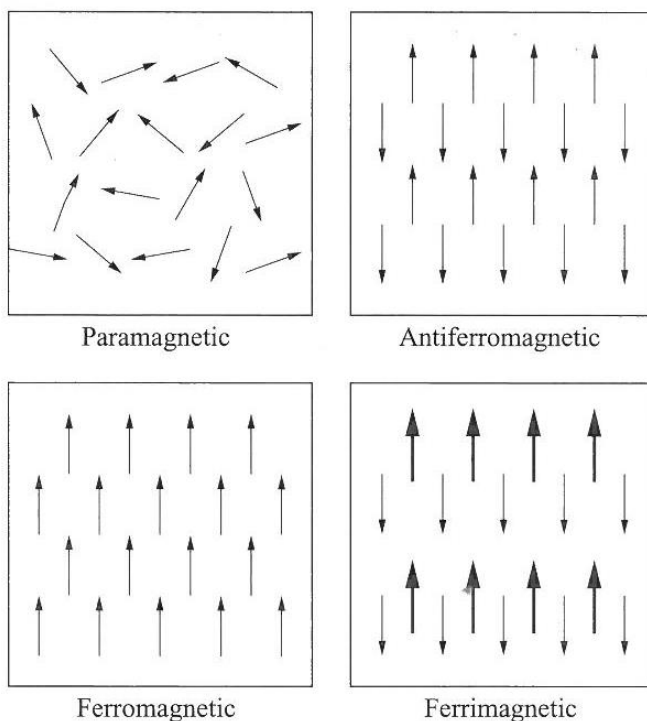
$$\chi = M/H \quad \text{Eq 1}$$

Specific changes in the susceptibility as a function of temperature mark phase transitions in the material. The various magnetic phases of a material range from well-ordered

ferromagnetism to disordered spin-glass and cluster-glass phases. Finally, the magnetic phases described here will be limited to the following: ferromagnetism, antiferromagnetism, paramagnetism, and ferrimagnetism.

Ferromagnetism is an ordered form of magnetism where the individual magnetic moments all tend to align in a single direction. In a similar manner, all of the moments comprising an antiferromagnetic material are aligned or anti-aligned with a specific direction. Each moment in such a material is anti-aligned, or pointing along the same line in the opposite direction, with each of its neighbors. In ferrimagnetic materials the moments are aligned as in the antiferromagnetic material but the strength of moments pointing in one direction is larger. In contrast to these ordered phases, in the paramagnetic phase, each moment rotates about in an unordered manner. A material in such a state would have no measurable magnetization in the absence of a magnetic field. The types of magnetism described above are shown in Figure 2.

The Griffiths Phase is found in the transition from the paramagnetic state to the ferromagnetic state. The temperature that this transition is complete is known as the critical temperature. The Griffiths Phase will be found just before the critical temperature. Characterizing and understanding the Griffiths Phase in  $\text{Mn}_{0.23}\text{TaS}_2$  and the 3-dimensional Ising model will be the focus of this study.

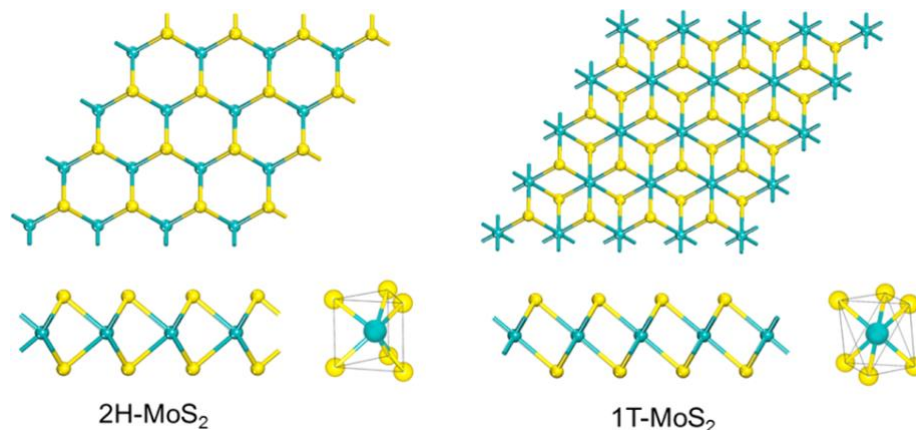


*Figure 2. Illustrations of four magnetic phases.<sup>[2]</sup>*

### **Literature Review**

Tantalum disulfide falls into the category of a low-dimensional solid. This is a result of the fact that the tantalum disulfide layers are bound together by weak forces. An entire solid crystal is composed of a large number of single layers, which by themselves are planar (two-dimensional). There are other materials that may be considered two-dimensional including graphite, mica, and many others. Tantalum disulfide is also a transition-metal dichalcogenide. This group of materials is typified by a layered structure where each transition metal atom is bound to six surrounding chalcogen atoms. (A chalcogen is an element from group 6 of the periodic table.) Molybdenum disulfide is a well-known material in this category. These materials have several interesting properties. Most notable is the variance in the materials' electronic band structure for each of its polytypes.<sup>[1]</sup> Each polytype references a different

orientation between consecutive layers of the material. Figure 3 shows two such polytypes for molybdenum disulfide. These materials also have interesting applications, such as the use of molybdenum disulfide as a lubricant.



*Figure 3. In the 2H polytype the chalcogenide atoms define the vertices of a triangular prism, while in the 1T polytype they define the vertices of an octahedron.*

The transition-metal dichalcogenides also have interesting electronic properties. The electronic properties present in a specific transition metal dichalcogenide depend strongly on the group from which the transition metal is taken. The Group IV dichalcogenides act as semiconductors and semimetals. The Group V dichalcogenides exhibit changes in their structure in response to periodic lattice distortion-charge density wave (PLD-CDW) transitions. The effects of these transitions depend on the polytype of the material. Of great interest is the competition between the superconducting phase and CDW in specific transition metal dichalcogenides.<sup>[2]</sup> Although the transition metal dichalcogenides have interesting properties in their unaltered state, much interest lies in properties of the intercalated forms of these materials.

A transition metal dichalcogenide is called intercalated when foreign atoms are introduced between layers of the original material. This is shown specifically for tantalum



disulfide on the left side of Figure 1. In addition, intercalating a magnetic atom such as manganese into a transition metal dichalcogenide allows the entire structure to have magnetic behavior.

In the paramagnetic phase, magnetic interactions between atomic moments within the material are weak in comparison with thermal effects. The moments in such a material rotate about their fixed positions in space due to random thermal activation. This disordered state occurs at temperatures higher than a critical temperature, below which an ordered state exists.<sup>[3]</sup>

Ferromagnetism is an ordered state of the magnetic moments of a material in which neighboring moments align with each other due to their mutual interactions. This neighbor-neighbor alignment is a long-range phenomenon that gives the material a spontaneous magnetization.

If the distance between neighboring moments is increased from the ferromagnetic state, neighboring moments will begin to become antiparallel with one another. This is the ordered state of antiferromagnetism. In this case no spontaneous magnetization should exist since each moment is nullified by its neighbor.<sup>[3]</sup>

Ising magnetic moments are moments that can only point in opposite directions along a single axis. Using a two- or three-dimensional lattice with Ising moments and only a fraction  $p$  of lattice sites occupied, Robert Griffiths showed theoretically that non-analytical behavior above the critical point will occur.<sup>[4]</sup> This behavior later became known as the Griffiths Phase and has now been observed in some materials in which disorder has been introduced. This disorder has been found to be essential since it shifts the ferromagnetic transition (Curie) temperature  $T_c$  and enables the system to form clusters of ferromagnetic regions that dominate the paramagnetic regime close to the transition.

The Griffiths Phase has been identified in several compounds, such as  $(\text{La}_{1-x}\text{Y}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ ,  $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-y}\text{Ga}_y\text{O}_3$ , and  $\text{La}_{0.4}\text{Ca}_{0.6}\text{MnO}_{2.8}$  [5,6,7]. The hallmark of Griffiths singularity is the downturn in inverse susceptibility below the Curie-Weiss line (eq 2) and an example can be seen in Figure 1.[5]

$$\chi = \frac{C}{T-T_c} \quad \text{Eq 2}$$

$(\text{La}_{1-x}\text{Y}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  exhibited properties of the Griffiths phase at  $x = 0.3$  and  $0.4$  but but no Griffiths phase for  $x = 0.5$  and  $0.6$ . This is similar to what has been observed in past research on the intercalated transition-metal dichalcogenide  $\text{Mn}_x\text{TaS}_2$  where only certain concentrations of manganese will result in the Griffiths Phase. The explanation of the observed effects of the Griffiths Phase is that there are ferromagnetic clusters in the paramagnetic region.[5,8] In the inverse susceptibility graph there is a downward deviation from standard paramagnetic (Curie-Weiss) behavior, which gets greater for smaller external fields. This is possible if there is short-range ferromagnetic ordering in the paramagnetic region.[1,9]

Robert Griffiths' original theory used the two-dimensional Ising model to predict the non-analytical behavior known as the Griffiths Phase. In order to support the claim that large ferromagnetic regions are dominating the system just above the critical temperature the Ising model was used to simulate a magnetic system that would replicate the experimental results. The Ising model is a way of simplifying the possible directions of the magnetic moments of atoms by constraining them to either point up or down. This allows for a system to be modeled without the need for complex mathematics to understand how the directions of individual spins are contributing to the magnetism of the entire system.

A valuable technique used in computational modeling is the Monte Carlo method which is used when there is a need for repeated random sampling. For a magnetic system this refers to

the lattice locations of atoms. For each step of the system as its temperature is decreasing it needs to come to equilibrium before lowering the temperature again. It's allowed to go to equilibrium because of the random sampling of lattice locations which get tested to identify if it is more stable for the magnetic moment to flip and point in the opposite direction or if it was more stable before the flip. If it is more stable after the flip that is the new orientation of the magnetic moment. If it was more stable prior to being flipped then the Boltzmann factor is used to decide if thermodynamics is going to cause the direction to flip. The Boltzmann factor is shown in eq 3, where  $\Delta E$  is the change in energy when the spin is flipped,  $k$  is the Boltzmann constant and  $T$  is the current temperature.

$$Z = e^{-\frac{\Delta E}{kT}} \quad \text{Eq. 3}$$

At low temperatures, then it is unlikely for the spin to be flipped when it is unfavorable, but at high temperatures it is likely to flip when it is unfavorable. These assumptions and mathematical models are what make up the basis for magnetic simulations.

### **Motivation**

Past results indicate that samples have exhibited Griffiths-like Phase behavior which will be explored more in this study for a  $\text{Mn}_{0.23}\text{TaS}_2$  bulk sample. The Griffiths Phase of the 3-dimensional Ising Model will also be investigated since it is the model on which Robert Griffiths based his theory. The magnetic characterization of  $\text{Mn}_x\text{TaS}_2$  and the Griffiths Phase of the 3-dimensional Ising Model will provide novel results and a basis for subsequent projects.

## **Methodology**

This project was completed through the following steps: sample fabrication, manganese concentration measurement, sample loading into Physical Properties Measurement System (PPMS), magnetic measurements using the PPMS, and data analysis using several well-documented methods.

The nanostructured samples were fabricated from elemental powders using long heating periods in glass ampoules. The heating process included a day at 125 °C, an increase to 700 °C, a hold at an annealing temperature, and finally a slow cooling (Kidd et al., 2012). Dr. Emilia Morosan worked to create the 23% nanostructured for this project but other samples used in past work were created by Dr. Laura Strauss.

Energy Dispersive X-Ray Spectroscopy (EDX) was performed on the samples to determine the relative concentrations of manganese, tantalum, sulfur, and impurities. These measurements were carried out by the members of Dr. Timothy Kidd's research group in the Physics Department. Such a measurement bombards the sample with electrons to produce X-rays of varying energy. The characteristic X-rays of the elements present in the material can then be identified. The relative intensity of the X-rays gives the relative amounts of each element. The error in such measurements is approximately  $\pm 10\%$ .

The samples were then inserted into delrin sample holders (approximately 146 cubic millimeters). Due to the fact that a measurement of the sample's mass is more easily made than that of its volume, subsequent susceptibility values were measured by per unit mass. Mass measurements were taken using a Mettler AE260 Delta Range Analytic Balance Scale.

The sample holders were secured to the ACMS module of the Quantum Design PPMS via a clear plastic straw. The system was sealed and the desired measurement sequence was

initiated from the control panel. Depending on the type of measurement, the sample was left within the system for 6-12 hours. The sample was then removed and placed in a desiccation vessel for storage. Data from any measurement was then saved and converted to the necessary format for analysis.

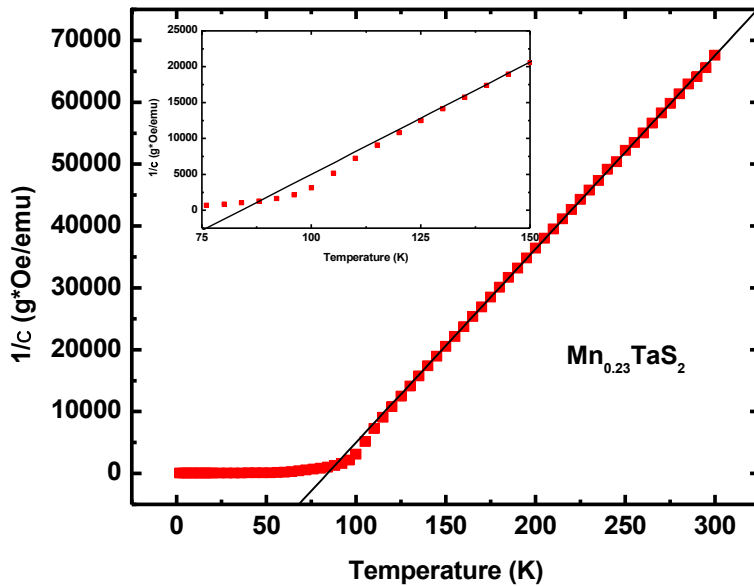
It is important to note that due to a lack of sample holders, samples were systematically moved from storage vial to sample holder and back to storage vial. Thus, if more data was required from a specific sample, then the mass associated with the new measurement would have been different from that of the original. In general, this was avoided simply by planning the measurements in advance; however, this was not always possible in the event of system maintenance and data collection for other experiments.

The data analysis methods included Arrott-Noakes and Curie-Weiss analysis. The first of these uses the Arrott-Noakes equation of state to extract fitting parameters from computer aided data fits. These parameters, so-called critical exponents, have allowed us to characterize the magnetic phase transitions of each sample. Curie-Weiss analysis has been used to determine the temperature at which each samples transitions from the paramagnetic state to an ordered state.

These methods have been implemented using *Origin 8*. This software was chosen due to its recognized ability for extensive data analysis, data plotting, and customizable data fitting. *Origin 8* acts as a more functional version of Microsoft Excel for complex fitting parameters. Each column in a sheet can easily be manipulated mathematically and plotted. *Origin 8* can then be used to determine the curve that best fits a data set. This allows one to extract values (such as those described in the theories section) from a given data set. *Origin 8*'s extensive data analysis tools are ideal for the data analysis required for this project.

## Results and Discussion

The  $\text{Mn}_{0.23}\text{TaS}_2$  nanostructured investigated in 2018 was first observed to have Griffiths like behavior when its inverse susceptibility was plotted against the temperature (figure 4). One sign of the Griffiths Phase is the deviation below the Curie Weiss line shown in black. The inset graph clearly shows the inverse susceptibility deviating below the Curie-Weiss line. Another characteristic of the Griffiths Phase is that the deviation becomes more intense as the external magnetic field is lowered. Figure 5 shows the same samples inverse susceptibility but under various magnitudes of external magnetic field strength. As the external magnetic field is lowered the deviation below Curie-Weiss becomes larger which is expected from the Griffiths Phase.



*Figure 4. Inverse Susceptibility of  $\text{Mn}_x\text{TaS}_2$  showing the downward turn characteristic of Griffiths Phase behavior*

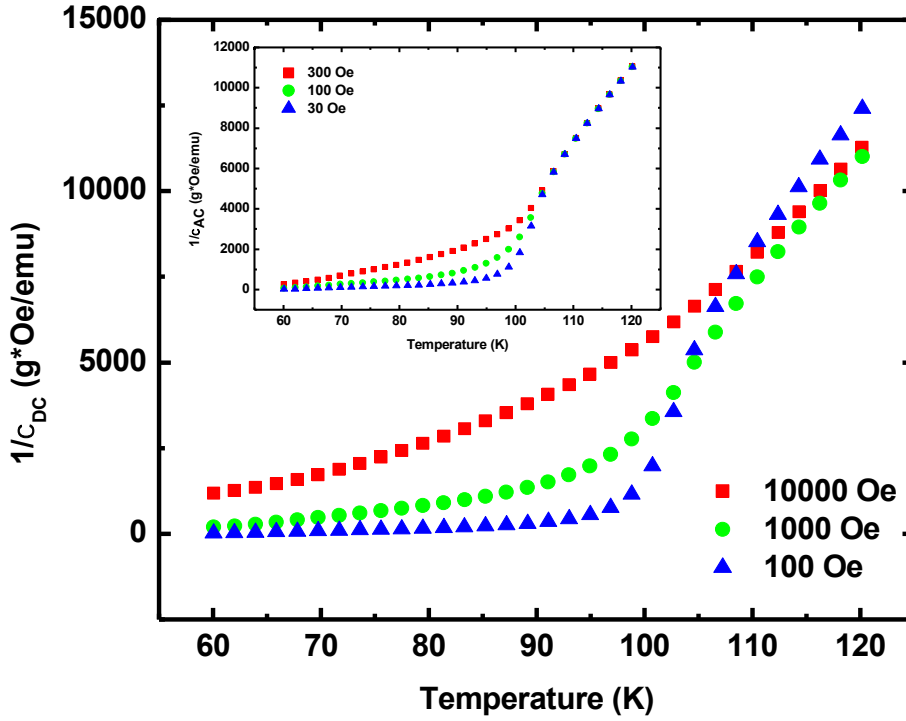


Figure 5. Inverse Susceptibility of  $\text{Mn}_x\text{TaS}_2$  at different values of external magnetic fields

Griffiths Phase Theory also predicts what is known as power law behavior. Power law behavior derives from the equation  $\chi = (T-T')^{-(1-\lambda)}$ . The equation can be rewritten or simplified to  $\ln(1/\chi) = (1-\lambda) * \ln(T-T')$ . In figure 6 is the natural log of inverse susceptibility vs the natural log of temperature minus a critical temperature 60K. Fitting a straight line to the Griffiths phase region gives us the slope which is equal to  $(1-\lambda)$ . For a typical material  $\lambda$  is 0 making the slope 1, the slope we got was .677 meaning our lambda value is .323. The higher the lambda value the stronger the Griffiths phase behavior.

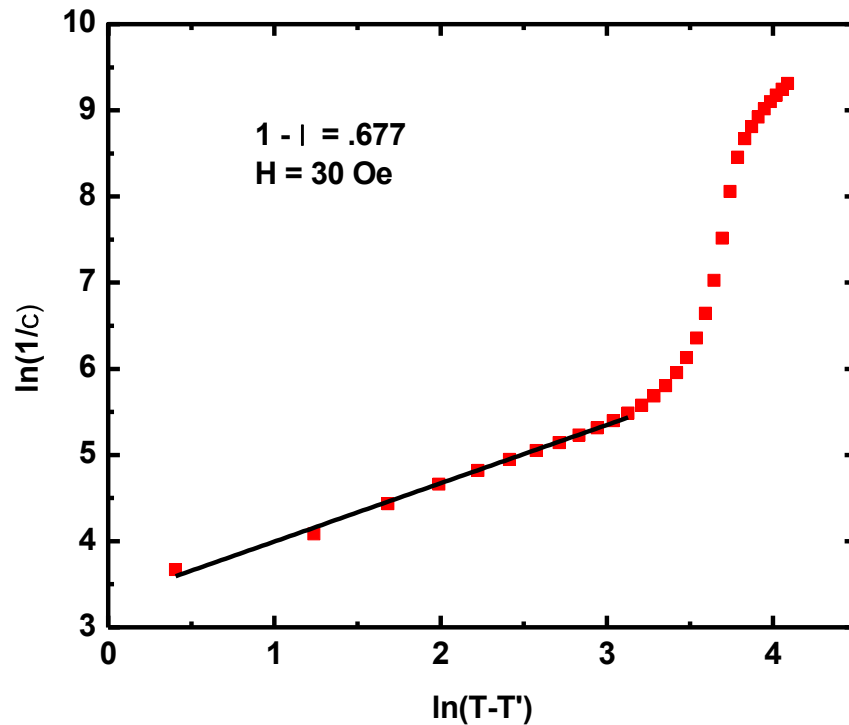


Figure 6. log-log plot of  $Mn_xTaS_2$

In Matlab previous students have written a program to determine the critical exponents beta and gamma of a material. The critical exponents tell you about the characteristics of the phase transition from paramagnetism to ferromagnetism for a material. The high field Arrott-Noakes data (figure 7) gives rise to typical beta and gamma values for the phase transition. However, the scaling plot (figure 8) produces an unusual value of delta where  $\Delta = \beta + \gamma$ . The delta from the Arrott-Noakes plot would be 1.96 which does not correspond to the value determined from the scaling plot of 2.6. This is most likely due to the lower field AC susceptibility data used in the scaling plot vs the high fields used in the Arrott-Noakes plot. We speculate that this field dependence of the critical exponents may be another manifestation of Griffiths phase behavior.



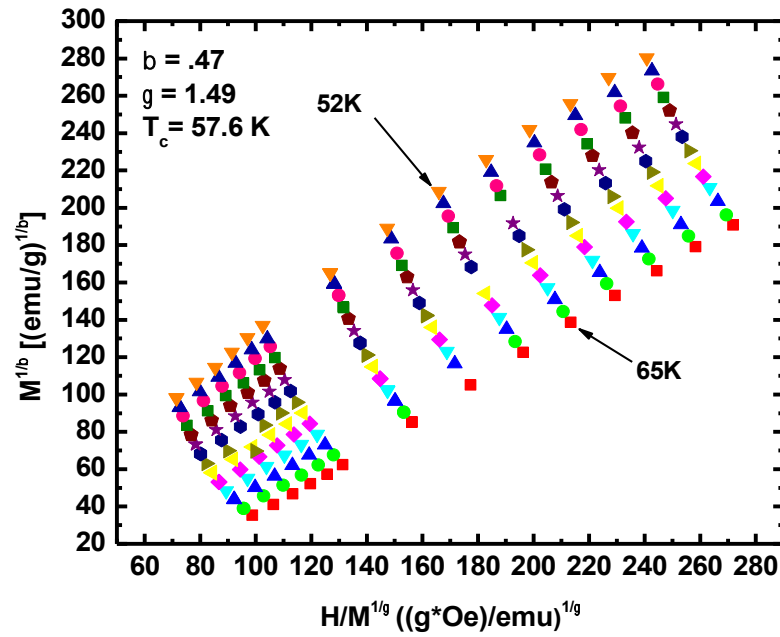


Figure 7. Arrot Noakes plot of  $Mn_{0.23}TaS_2$

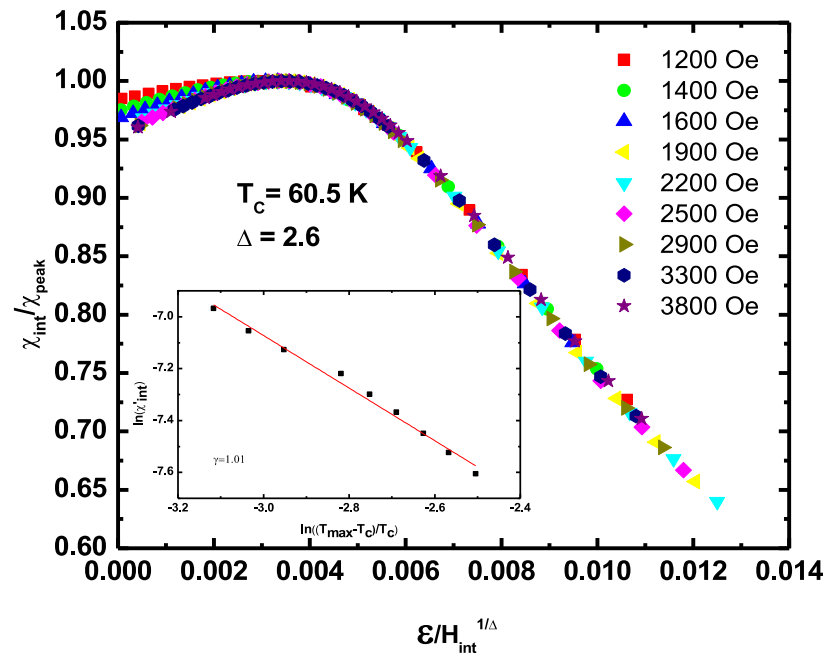


Figure 8. Scaling Plot of  $Mn_{0.23}TaS_2$

The results of the 3-dimensional Ising Model show that the computational model correctly models a magnetic system. Figure 9 shows the Curie-Weiss fitting of the inverse susceptibility graph for a 20x20x20 lattice that is only 95% filled. In the paramagnetic regime the Curie-Weiss line closely fits the inverse susceptibility similar to what was seen in the experimental inverse susceptibility. A downward deviation was not found since the proper parameters were not used to manifest a Griffiths-like Phase.

In order to see a downward turn greater disorder needs to be introduced (lower % filled lattice) at a weaker external field. Another possible limitation is how small of a system was modeled. A lattice size greater than 20 may be required in order to have the possibility of generating clusters that will dominate the system near the critical temperature.

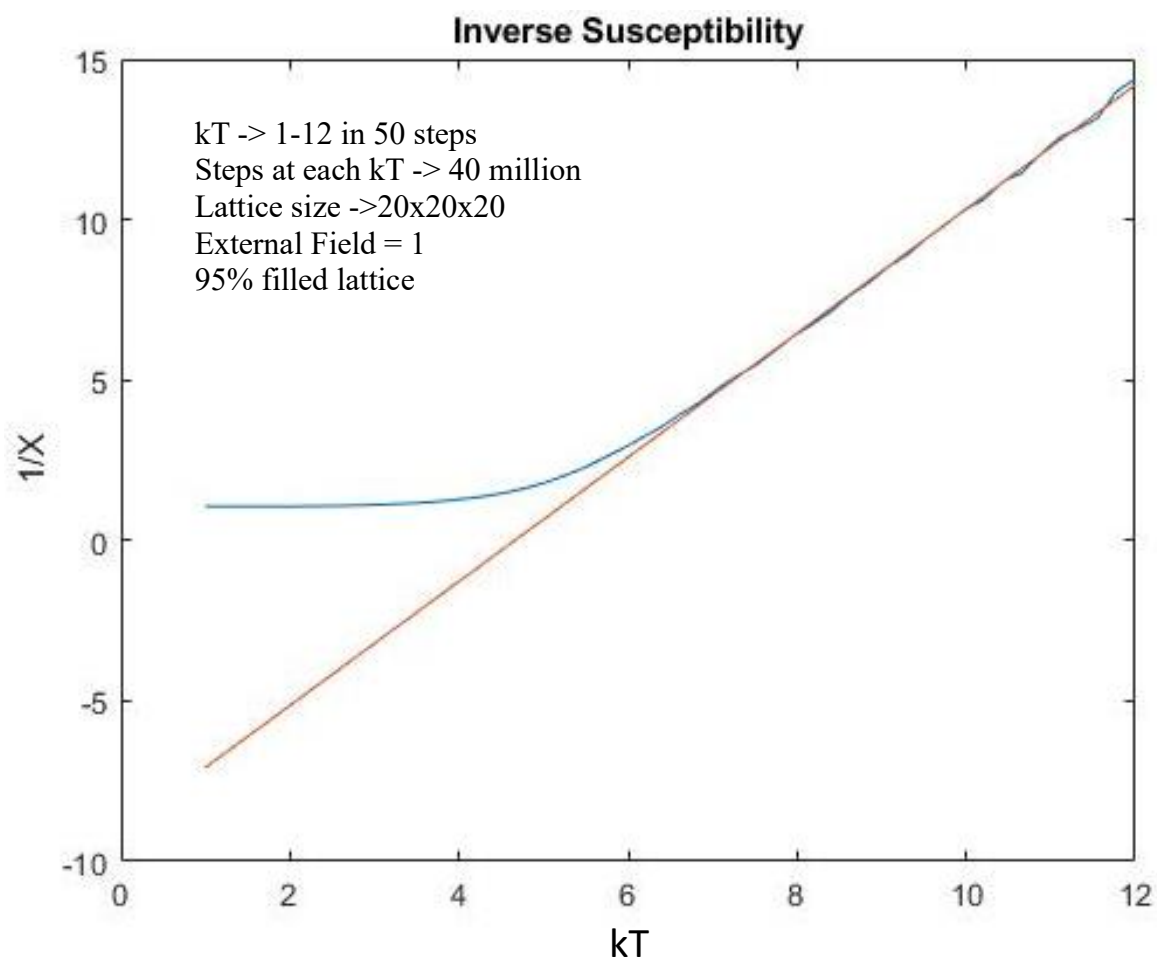


Figure 9. Inverse Susceptibility of a 20x20x20 lattice

## **Conclusion**

The crystalline bulk  $\text{Mn}_{0.23}\text{TaS}_2$  was shown to have Griffiths-like behavior due to the downturn in the inverse susceptibility graph and the atypical value of  $\lambda$  showing non-analytical behavior. The deviation below Curie-Weiss line suggests that the system is ferromagnetically aligning faster than what is predicted by Curie-Weiss law. This can be explained by large ferromagnetic domains that dominate the system near the critical temperature. The critical temperature was found to be 60.5K with the Griffiths-like phase behavior beginning around 110K. The comparison of samples with different manganese concentration and structure will be useful in looking for new materials that exhibit the Griffiths phase. The computational model was successful in modeling a magnetic system based on Robert Griffiths original theory. The next step is to introduce greater disorder in the system and increase the system size to provide an opportunity for large ferromagnetic domains to form. Once the correct parameters that cause the Griffiths phase for the computational model are found it will be valuable to use to predict different ways of causing the Griffiths phase.

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